

PREPARATION OF SOME CHROMIUM AND IRON SCHIFF BASE COMPLEXES AND THEIR STUDIES AS A COLOURING PIGMENTS IN COATING INDUSTRY.

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ABSTRACT:

Schiff base complexes based on chromium and iron metals have been widely used as metal complex pigments in coating industry. The Schiff base ligand is prepared by the condensation of aromatic amine namely Ortho-anizidin with selected aldehyde namely N,N Dimethyl-Para- amino-benzaldehyde and the microwave technique was used for the preparation of ligand and its metal complexes. The characterization of ligand and its metal complexes were studied using elemental analysis, ¹HNMR, spectral UV-Visible reflectance, infrared, magnetic properties, and thermal gravimetric analysis (TGA). The physical properties of solid complexes showed their stability to be formulated as pigments in anticorrosive paint formula, also the mechanical, color properties, corrosion resistance of dry paint films were also examined and showed excellent mechanical, corrosion resistance and color stability.

Keywords: Transition metal complexes, Schiff bases, Pigments, paints, corrosion resistance

INTRODUCTION

The Interest in the synthesis and characterization of transition metal complexes of schiff bases containing nitrogen and oxygen donor's atoms has increased manifold in the recent time. The Schiff base ligands are considered to be good chelating agents, especially when -OH functional group is close to the azomethine group. Schiff bases are a special class of ligands with a variety of donor atoms exhibiting interesting coordination modes towards transition metals, and azomethine linkage is responsible for the biological activities. The Schiff bases derived from various amines have been widely investigated and find applications in biomimetic catalytic reactions, materials chemistry and industry. Schiff base complexes have also gained attention as stereochemical models in transition metal coordination chemistry due to their structural variety. A number of transition metal schiff's base complexes have been studied extensively showing variable coordination geometry and flexible oxidation states with ligating system as varied as bidentate, tridentate, tetradentate and multidentate. Some of them are key points in the development of inorganic biochemistry, catalysis and industrial purpose [1-5]. Metal complex pigments are mainly used in paints, and the products are fast enough to be applied especially in industrial finishes. Some representatives, particularly azomethine copper complex pigments, are very

good weather fastness, which makes them suitable candidates for automotive finishes. High transparency in combination with good weather fastness is an asset for use in metallic finishes. It is not uncommon for metal complexes to lose much of their brilliance in white reductions. Some are also recommended for use in architectural paints, especially for emulsion paints. Besides, metal complex pigments are also used in printing inks as well as in other areas of application [6]. In the present work some Schiff base complexes based on chromium and iron metals were prepared and used as a pigments in paints industry.

Experimental

MATERIALS AND INSTRUMENTS

All chemicals and solvents used were of BDH and sigma-Aldrich of analar quality and used without further purification. ¹H NMR spectra in D6-DMSO with TMS as internal standard were obtained from a Jeol- FX-90Q Fourier NMR spectrometer and the Fourier transform infrared (FTIR) spectra were recorded on a single-beam spectrometer (Bruker, Vector 22, Germany) with a resolution of 4 cm⁻¹. Elemental analysis for carbon, hydrogen and nitrogen were determined by Perkin-Elmer, An electron relectence spectra were recorded on Shimadzu UV-2600/2700, and thermal Gravimetric analysis (TGA) were done using Shimadzu's TGA-50/51

Preparation of N,N' bis(4-dimethyl amino benzalene)3,3 Dimethoxybenzidine (ligand)

The ligand (L) was prepared by using microwave method [Kenwood MW589, 1450 Watt, 50 Hertz, 230 Volt] in which the 3,3-dimethoxy anisidine and Para-Dimethylamino-benzaldehyde are mixed in equal molar ratio and grounded very well in ceramic mortar and transferred to porcelain crucible and then the crucible put in microwave for 3 -5 minutes and high yield (98%) of the ligand is obtained with the chemical formula $C_{32}H_{34}N_4O_2$ and have chemical structure as in Scheme 1.

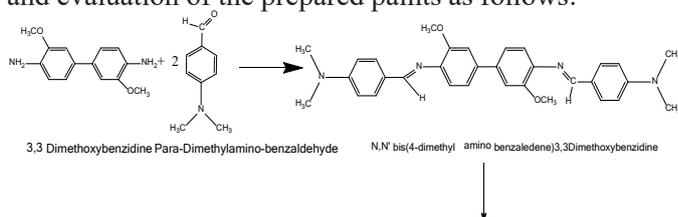
Preparation of solid complexes and their evaluation as a pigments

All the complexes were prepared by mixing equal molar ratio amounts of ligand and the metal(III) chloride [$M = Fe^{III}, Cr^{III}$] in porcelain crucible, then the crucible put in the microwave for 3 – 5 minutes and the resulting complexes were removed from microwave and cooled (Figures 1, 2) [7].

The prepared complexes were evaluated as pigments and the following tests were performed according the standard test methods of the American society of testing and materials (ASTM):(i) oil absorption (ASTM D:281-95, 1995) (ii) hydrogen ion concentration (pH value) (ASTM D:1583-01, 2001), (iii) bleed test (ASTM D:279-87, 1997), (iv) fineness of dispersion (ASTM D:1210-96, 1996), (v) Moisture content (ASTM D:280-95, 1995).

Paint preparation, evaluation and application

The paints were prepared by employing high stirring mixer and then they were introduced into a cold roll mild steel panels by using spray gun in a closed cabinet to give a dry paint film. The pigment is formulated in anticorrosion paint formula based on epoxy resin as anticorrosive binder according to conditions stated in Table 1. Various methods have been applied for testing and evaluation of the prepared paints as follows:

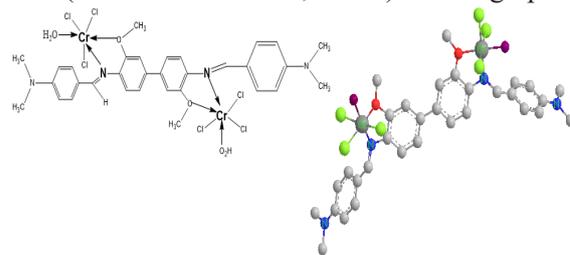


Physical and mechanical tests

A variety of physical and mechanical evaluations of the paint films were carried out on prepared steel panels (ASTM D:609-00, 2000) such as (i) determination of the dry paint film thickness (ASTM D:4138-07, 20001); (ii) measuring of adhesion using adhesive tape (ASTM D:2794-93, 1999); (iii) resistance of organic coatings to the effects of rapid deformation (impact) (ASTM D:3359-97, 2005).Scheme 1. The chemical structure of ligand

Corrosion tests

The coated steel panels were put in a salt spray cabinet at a temperature of 35°C, a moisture of 100% and a test solution of 5% NaCl concentration for 500h (ASTM B117-03, 2003). The films were then examined for any defects such as rusting (ASTM D:714-07, 2007), blistering (ASTM D:610-01, 2001), and scribe failure (ASTM D:1654-92, 2000). Photographic



to penetrate the panel to examine adherence of paint over the painted area.

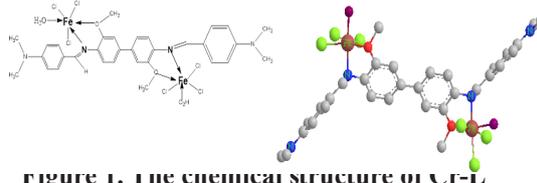


Figure 1. The chemical structure of Cr-L

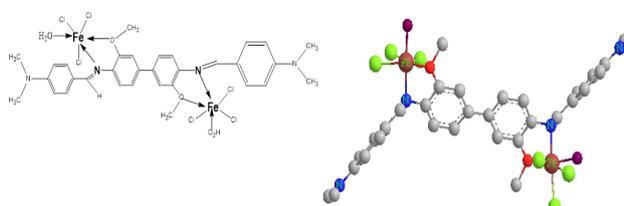


Figure 2. The chemical structure of Fe-L

Determination of chromatic characteristics

The chromatic characteristics of a substance are defined by the colorimetric or chromaticity coordinates: clarity (L^*), red/green color component (a^*), and blue/yellow colour component (b^*); and by its derived magnitudes: chroma (C^*), tone (H^*) and chromacity [(a^*, b^*) or (C^*, H^*)]. Overall colorimetric difference between two samples ΔE^* is defined according to the following mathematical functions:

$$\Delta E^* = (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 = (\Delta L^*)^2 + (\Delta C^*)^2 + (\Delta H^*)^2$$

Where ΔL^* is the change in color clarity, Δa^* is the change in the red or green tone, H^* is color tone, C^* is chroma (colors homogeneity) and ΔE^* is overall differences of the color of paint film before and after the corrosion test.

The color measurements were obtained by using The X-Rite RM200QC instrument, which is Imaging Spectro-colorimeter bridges for the gap between color appearance and material color. The device is automatically measuring the above mentioned parameters (ΔE^* , ΔL^* , Δa^* , Δb^* , ΔC^*).

Table 1. Anticorrosion paint formula

Ingredients	Conc. (%)
Epoxy resin	25.5
Silanol functional silicone resin (dispersing agent)	0.2
N-Butanol	6
Aluminum silicate	20
$Mg_3Si_4O_{10}(OH)_2$ (talc powder)	13
$BaSO_4$	12
Prepared complex	5
Xylene	2
Fumed silica	2
Organic clay	0.7
Polymethyl siloxane (antifoaming agent)	0.1
Polyether copolymers (leveling agent)	0.2
Methyl ethyl ketone	13.3
Curing agent (polyamide)	12.5

(1) Epoxide Equivalent Weight (g/eq): 430, Density @ 25°C (g/ml): 1.09, Non-volatile Content (wt%): 74 – 76.

RESULTS AND DISCUSSION

All the analytical, physical and spectroscopic data of the Schiff base ligand and its isolated metal complexes are given in Tables 2 and 3. The complexes are air stable (not contains moisture when stored for a long time) and are soluble in DMF & DMSO.

*Infra-red spectra**IR of ligand*

The positions of the significant IR bands of N,N' bis(4-dimethyl amino benzaldehyde)3,3 Dimethoxybenzidine (L) and its metal complexes are summarized in Table 3. The IR spectra of ligand (L) show a strong band at 1603 cm^{-1} assignable to $\nu(C=N)$ of the azomethine. The observation of this band confirms the formation of the azomethine linkage. The ligand also has a strong band in the region 770–824 cm^{-1} corresponding to the out-of-plane deformation of the aromatic rings [8,9]. The observation of strong bands at 1238 cm^{-1} is taken as an evidence for the existence of $\nu(C-N-C)$.

IR of Cr^{III} and Fe^{III} complexes

The IR spectral data of chromium complex indicates that the ligand (L) behaves in a tetradentate manner with two Cr^{III} and Fe^{III} metal ions via two azomethine and two methoxy groups. This behavior is supported the following evidences: (1) The negative shift of the azomethine groups to lower wave number together with the appearance of new bands assigned to ν_{M-N} vibrations suggested the involvement of this group in bonding with the metal ions. On the other hand, the splitting observed for $\nu_{C=N}$ with metal ions suggests the presence of two types of azomethine groups, (2) The appearance of new bands in the range 501-507 and 353-371 cm^{-1} , attributed to ν_{M-O} and ν_{M-N} vibrations supporting the participation of the nitrogen atom of the azomethine group and oxygen atom of methoxy group of the ligand in the complexation with the metal ions, (3) Finally, The bands observed at 308–325 cm^{-1} attributed to $\nu(M-Cl)$, elucidate the presence of

Cl ions in the proposed structures [10-14].

¹H-NMR spectra of the ligand

The ¹H-NMR spectra of the ligand were recorded in DMSO. The proton NMR spectrum of the ligand as shown in Figure 3, Table 2, indicates the appearance of a singlet signal in the range of 3.86– 3.89 ppm due to the presence methyl protons. In the aromatic region; a few doublets and some overlapping doublets/multiplet are observed at range 6.7 – 7.7 ppm. These signals are due to the protons of benzene rings. The signals due to azomethine protons (-CH=N-) appeared as a singlet at 8.4 ppm [15,16].

Electronic Spectra and Magnetic properties

The electronic spectra data of ligand (L) (Figure 4, Table 3) showed the bands that observed at 344 and 380 nm which are assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the ligand, usually $n \rightarrow \pi^*$ transitions occur at lower energy than $\pi \rightarrow \pi^*$ transitions [17]. The magnetic and electronic spectra data of Cr^{III} complex (Figure 5, Table 3) shows μ_{eff} value 4.1 B.M corresponding to the presence of three unpaired of electrons and the complex exhibit maximum band at 584 nm due to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (F) transition which is consistent with octahedral geometry [18,19]. The μ_{eff} value 5.96 B.M obtained for the Fe^{III} complex is in good agreement with the octahedral geometry and the electronic spectra of iron complex (Figure. 6, Table 3), appears maximum band at 637nm may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (P) transi-

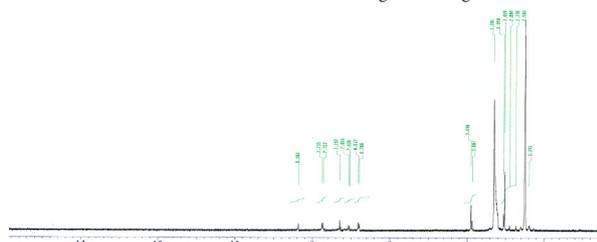


Figure 3. ¹H NMR spectra of ligand

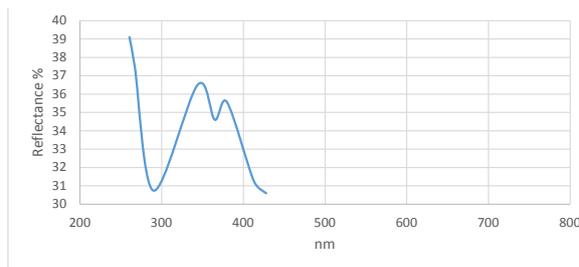


Figure 4. UV-Visible reflectance spectra of ligand

tion [20,21].

Thermal studies

Thermal analysis of all complexes was carried out by the TGA, DTA techniques. The experimental results revealed that the degradation occurred in multiple stages, following a complex mechanism (Figures 7-8). For each stage, the kinetic parameters and thermogravimetric characterization have been estimated. The thermal behavior of all complexes explains as followed: the TG curves follows the decrease in sample mass with an increase in temperature. In the present investigation, heating rates were suitably controlled at 10 °C/minute and mass loss followed up to 25 – 1000 °C. The chromium complex slowly studied the decomposition between 25 and 450 °C. The first mass loss occurring at temperature >191 °C attributed to the removal of two coordinated H₂O molecules. The mass loss occurring at temp 191 – 232°C correspond to the decomposition of three molecules of HCl, then mass loss at temp 232-450 is attributed to the decomposition stages of the ligand molecules and the remaining HCl molecules in the complex. The final product of the thermal decomposition at 450 – 1000 °C might be referring to the presence of metal oxide. On the other hand, the iron complex studied the decomposition between 25 and 610 °C. The first mass loss occurring at temperature in the range of 25-235 °C attributed to the removal of coordinated H₂O meanwhile the mass loss occurring at temp 235 – 610°C correspond to the decomposition of organic ligand & HCl molecules. The final product of the thermal decomposition at 610 – 1000 °C might be referring to the presence of metal oxide [22].

Evaluation of the prepared complexes as pigments for paint application.

Physical properties of the prepared complexes

The prepared complexes are evaluated as pigments before using in the corrosion resistance paints formulations and the following test methods (Table 4) cover the procedures for determining certain properties of pigments according to ASTM Standards.

Based on the results summarized in Table 4,

Table 2. Analytical, physical and spectroscopic data of the Schiff base ligand and its related metal complexes

Compound	M.p(°C), colour	Theoretical (found) %		Metal content % (found)	¹ H NMR Chemical Shift (δ p.p.m.)
		C	N		
Ligand (L)	250, lemon yellow	75.9 6.8 (75.2) (6.3) (6.3)	7		8.4 (CH=N,s,2H), 3.89 (OCH₃), 6.7-7.7 (Ar-H, ring)
[Cr₂(L)(Cl)₆(H₂O)₂] Bluish red	>370,	44.7 4.4 (43) (6.6)	6.5 5	13 (12.8)	
[F₂(L)(Cl)₆(H₂O)₂] Brown	>370,	44.5 4.7 (46) (4.4)	6.5 6.9	12.9 (12)	

it was noticed that all the synthesized complexes are alkaline in nature based on pH values. It is clear that the oil absorption values of chromium complex were the lower than iron complex. As the oil absorption value increased, more binder is needed to completely wet the pigment and form a homogeneous paint film and vice versa.

The moisture contents in all complexes are neglectable. The fineness (degree of dispersion) test covers the measurement of the degree of dispersion (commonly referred to as “fineness of grind”) of the pigment in a pigment-vehicle system such as liquid coatings and their intermediates. The fineness results of the samples indicated that all prepared complexes are highly dispersed in pigment-vehicle (ASTM D:1210-96,1996). The bleeding test determines the amount of color produced when the pigment is in direct contact with different solvents. The bleeding tests implying a high degree of stability of the prepared pigments. Moreover, the bleeding results indicated that there is no bleeding (none perceptible color) [23].

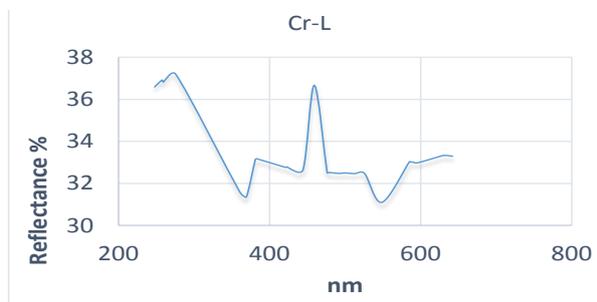


Figure 5. UV-Visible reflectance spectra of Cr-L

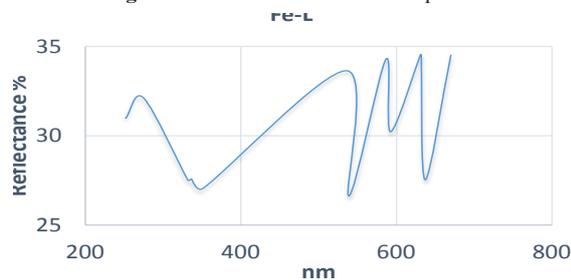


Figure 6. UV-Visible reflectance spectra of Fe-L

[H= Hegman (fineness unite), T=Toluene, EG=Ethylene Glycol, BAac =Butyl Acetate, N.B=Normal Butanol, MEK=Methyl Ethyl Ketone, N= none perceptible color]

Table 3. Significant IR, UV-Reflectance and magnetic data of Schiff base ligand and its metal complexes

Compound	$\nu(\text{OH})$ $\nu(\text{C-N-C})$ $\nu(\text{M-O})$ $\nu(\text{M-Cl})$	$\nu(\text{C=N})$ $\nu(\text{C-O})$ $\nu(\text{M-N})$	λ max, nm (assignments)	$\mu_{\text{eff.}}$ (B.M)
Ligand (L)	3481 1238 -	1603 1020 -	344 ($\pi \rightarrow \pi^*$) 380 ($n \rightarrow \pi^*$)	
$[\text{Cr}_2(\text{L})(\text{Cl})_6(\text{H}_2\text{O})_2]$	3321 1345	1599.6 1018 501	308,330 584 (${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{F})$) 350 (${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$)	4.1
$[\text{Fe}(\text{L})(\text{Cl})_6(\text{H}_2\text{O})_2]$	3308 1335	1599 1130 507 371	325 637 (${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$) 589 (${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$) 351 (${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$)	5.96

Physical and mechanical properties of the painted films:

Based on the results of the physical and mechanical properties of dry paint films with & without prepared complexes given in Table 5, the prepared films exhibit high film performance when the coating of 120 μm thickness was applied to the surface. The impact test shows the high resistance of the paint film to the rapid deformation by applying heavy weight directly to the surface (ASTM D:3359-97, 2005), also the adhesion of paint layer to the metal was excellent (5A) after the adhesion test (ASTM D:2794-93, 1999).

Table 5. Results of Impact, Adhesion and Dry film thickness for painted films based on the pre-

pared complexes.

Metal complex	Impact	film thickness (μm)	Adhesion
	Dry		
Blank sample	Pass	120	5A
Cr-L	Pass	120	5A
Fe-L	Pass	120	5A

5A no peeling or removal.

Corrosion resistance of the painted films

Anticorrosive protection by paints has recently been described as being a combination of a physical barrier, a chemical inhibitor, and an electrical resistor. Pigments are incorporated in paints in order to enhance the barrier effect and give the desired color with no effect on the

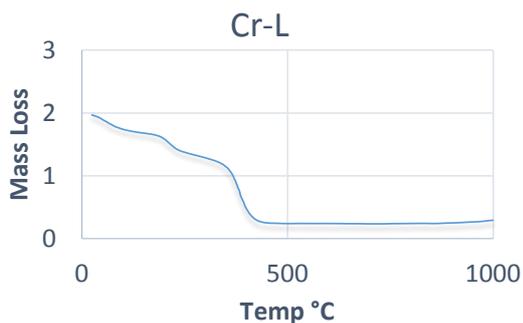


Figure 7 TGA chart of chromium complex

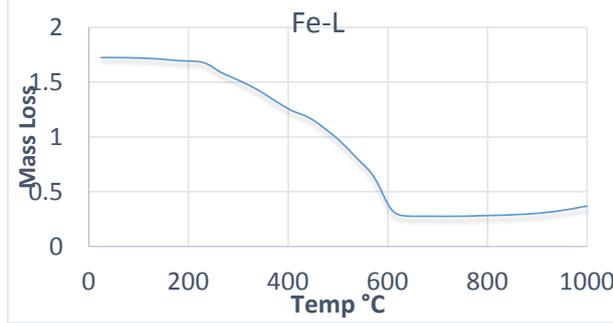


Figure 8. TGA chart of Iron complex

Table 6. Results of corrosion resistance of painted films based on the prepared complexes.

Painted film	Blistering		Scrub failure(mm)		Rust grad
	Size	Frequency	Area Failed %	Rating Number	
Blank Sample	9	F	1	9	9
Cr- L	8	F	1	9	8
Fe- L	9	F	1	9	8

Table 7 Results of chromaticity coordinates of painted films before and after salt spray test (ASTM B-117).

Complex	Before salt spray test					After salt spray test					ΔE
	L*	a*	b*	C*	H*	L*	a*	b*	C*	H*	
Cr ^{III} -L	73.9	-14.3	13.1	19.4	137.5	74	-14.2	13	18.7	137.3	0.8
Fe ^{III} -L	33.6	17.4	34.1	38.3	63	33.8	17.1	34.1	38.1	63	0.8

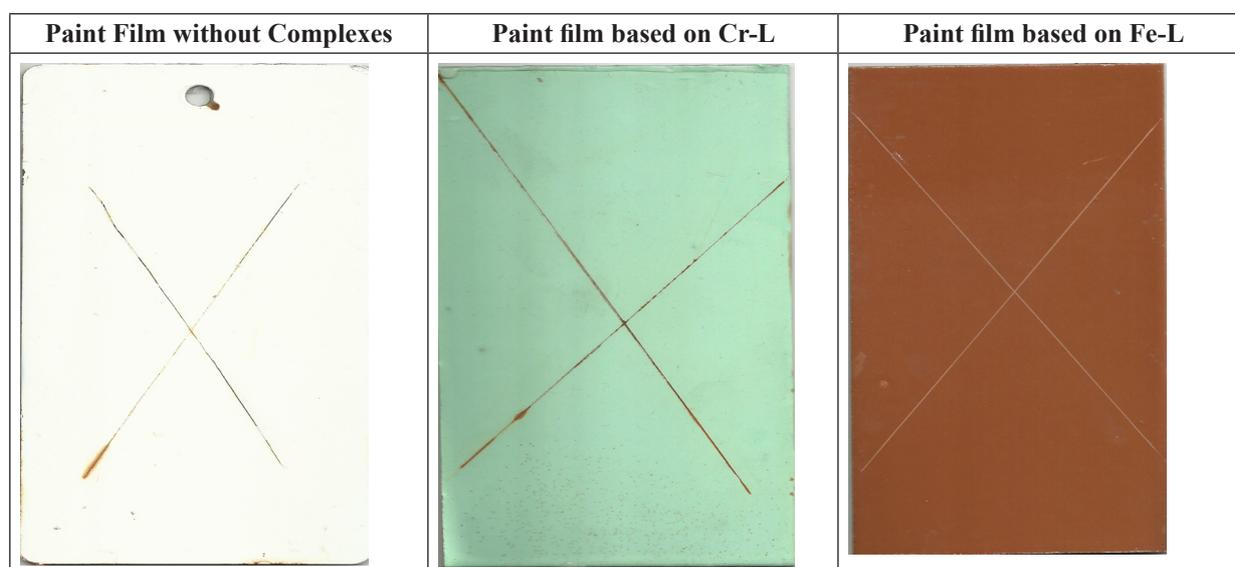


Figure 9. Photograph of the painted films with and without the prepared complexes after salt spray test (500 h of B-117).

properties of paint's film. In the current work the corrosion properties of the paints based on the prepared complexes were studied to investigate if there is any effect of the prepared complex on the paint's film.

The results of corrosion resistance of the blank film and the painted films based on the prepared complexes are given in Table 6. Figure. 9 shows the photo of the painted films after salt spray test. The film thickness of the films ranges from 100 μm to 120 μm .

The blistering size is graded from 10 to 0, where 10 represents no blistering where 0 represents the largest blister. Blistering frequency is denoted by F, M, MD and D (few, medium, medium dense and dense). Painted, or coated, specimens subjected to a corrosive environment are also evaluated by recording the average (mean) maximum and minimum creep age from the scribe mark. Scribe failure is also rated on a scale from 10 to 0, with 10 being zero (mm) from the scribe mark and 0 is 16 (mm) from the scribe mark. Rust grade 10 represents no rusting or less than 0.01% of surface rusted; rust grade 0 represents approximately 100% of surface rusted.

Chromatic characteristics of painted films

The results of color characteristics of the painted films based on the prepared complexes before and after salt spray test are listed in Table (7). The results shows that the ΔE values for the painted films after salt spray test were less than one, which indicates no change in the color of the films before and after exposure to the corrosion conditions which is referring to the color stability of the painted films, hence explains the stability of the prepared complexes when they used as anticorrosive metal complex pigments [24].

Conclusion:

The organic ligand and its metal complexes were successfully prepared by microwave method and high yield is obtained.

The physical properties of the prepared complexes (Fineness, Moisture content, bleeding), signified good performance materials.

The prepared metal complexes can be used as pigments in the field of anticorrosion paints with no side effects on the paint formula.

The Paint films based on the prepared complexes exhibited good mechanical properties (impact, adhesion).

The Paint films based on the prepared complexes exhibited good corrosion resistance properties.

There was no difference in the color properties of the painted films before and after corrosion conditions which is referring to the stability of the color of the prepared complexes.

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